VII → VIII

Summary

It has been shown that the determination of the position of the wave length of maximum absorption for the intense band in the absorption spectra of α,β-unsaturated ketones reveals the extent of substitution of the carbon–carbon double bond in an α,β-unsaturated carbonyl system.

The power of the method as a tool in structure determinations is indicated and exemplified.

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Photolysis of Biacetyl in the Near Ultraviolet

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Investigations in recent years have shown that biacetyl is a product of the photolysis of various compounds, such as acetone,[1] methyl ethyl ketone,[2] and acetaldehyde.[3] If any of these reactions is allowed to proceed to an appreciable extent, decomposition of the biacetyl formed may tend to obscure the results of the primary reaction. The investigation herein described was undertaken to study quantitatively the photolysis of biacetyl in the vapor state and to make a comparison with results of recent investigations on the thermal decomposition of this compound.[4]

The effect of ultraviolet light on biacetyl has received little attention to date. In aqueous solutions it is reported to give acetaldehyde and acetic acid.[5] In benzene and ether solutions it was found that no gaseous products are evolved.[6] In a qualitative experiment[5] on the vapor at 100° and atmospheric pressure, full exposure to an unfiltered arc gave gases reported to be carbon monoxide and ethane in a volume ratio of 2 to 1. Considering the complexity of the photolysis of the homolog glyoxal,[7] it was felt that the reaction of biacetyl might be more complex than previously supposed. That such is the case is shown by the large percentage of methane found in the products reported in the present paper.

(1) Spence and Wild. *Nature*, **138**, 206 (1936): *J. Chem. Soc.*, 352 (1937).

(2) Ells and Noyes. THIS JOURNAL, **60**, 2031 (1938).

(3) Blacet and Blaedel, *ibid.*, **62**, 3374 (1940).

(4) (a) Rice and Walters. *J. Chem. Phys.*, **7**, 1015 (1939): (b) Walters. THIS JOURNAL, **62**, 880 (1940).

(5) Porter, Ramsperger and Steel, *ibid.*, **45**, 1827 (1923).

(6) Bowen and Horton. *J. Chem. Soc.*, 1505 (1934).

(7) (a) Norrish and Griffiths, *ibid.*, 2829 (1928): (b) Blacet and Moulton, THIS JOURNAL, **63**, 868 (1941).

Experimental

The photochemical apparatus was quite similar to the one used in a study of the photolysis of crotonaldehyde at elevated temperatures.[8] Products not condensed at dry-ice temperature were treated with slightly moist potassium hydroxide beads to remove any biacetyl and ketene present. The remaining gases were then analyzed by micro methods. Quantum yields reported are based upon analyses for carbon monoxide in the permanent gas. All results reported represent the averages of from 2 to 5 determinations on aliquot portions of the sample.

Except at the lowest pressures, the reaction was not allowed to proceed more than about 2 or 3% toward completion—as determined from the amount of carbon monoxide produced. It was found that no corrections for thermal decomposition were necessary at these temperatures, in agreement with the observations of Walters,[4b] who could detect no decomposition below 346°.

Beer's law was found to hold within experimental error at room temperature. Assuming that it applies at higher temperatures and that the absorption coefficient is independent of temperature, it was possible to calculate[8] the absorption at elevated temperatures from a measurement of the arc intensity through the cold cell.

Experimental Results

In the present paper quantum yields have been calculated on the basis of molecules of carbon monoxide produced per quantum absorbed. It is recognized that if, as in the thermal decomposition, a molecule such as ketene is produced, not all of the reacting biacetyl molecules are accounted for by the carbon monoxide and Φ is low correspondingly. Usually runs were made in series such that only one factor varied at a time. Fig. 1 shows directly the increase of Φ with rise of temperature. Further, it shows that at any one temperature Φ increases with decreasing wave length.
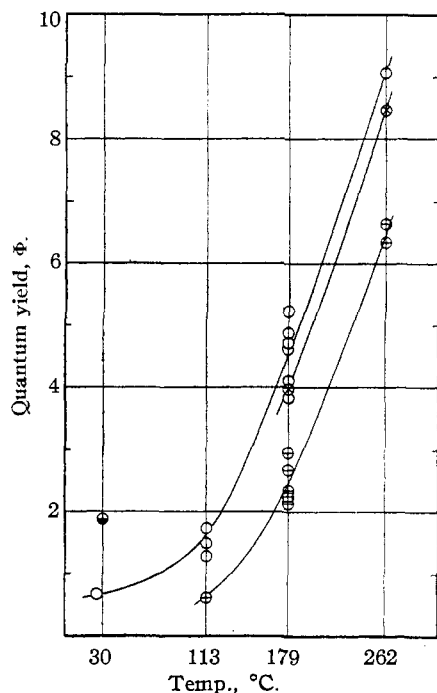
(8) Blacet and LuValle. *ibid.*, **61**, 273 (1939).

Fig. 1.—Effect of temperature on quantum yield: ●, λ = 2380 Å., P = 39 mm., $I_{abs.}$ = 1.27 × 10^{14} quanta/sec. O, λ = 2654 Å., P = 22–44 mm., $I_{abs.}$ = (1.19 – 5.06) × 10^{14} quanta/sec. ⊗, λ = 3130 Å.. P = 40 mm., $I_{abs.}$ = (1.32 – 1.56) × 10^{14} quanta/sec. ⊖, λ = 3660 Å., P = 12–40 mm., $I_{abs.}$ = (1.66 – 9.58) × 10^{14} quanta/sec.

Analysis of the data proves that there is a decrease in Φ with an increase in absorbed intensity at both λ 2654 and λ 3660. Within limits of experimental error the numerical values for quantum yields can be obtained from this figure.

The gaseous products of photolysis contained carbon monoxide, methane, ethane, and traces of hydrogen and unsaturated compounds. In Table I are listed analyses of four typical runs showing variations in composition of the gas with wave length and temperature. Also included are some average data on the thermal decomposition.[4a] With the exception of the low temperature run, 7, each analysis made showed the percentage of methane to be greater than that of the ethane; the average ratio was of the order 3 to 1. Other factors being constant, the CH_4/CO ratio increases rapidly with rise in temperature. Our data also show that this ratio decreases slightly with increased light intensity.

Figure 2 is a plot of the ratio CH_4/CO against quantum yield for all experiments for which both of these data were available. Composition of the products is definitely a function of factors affecting
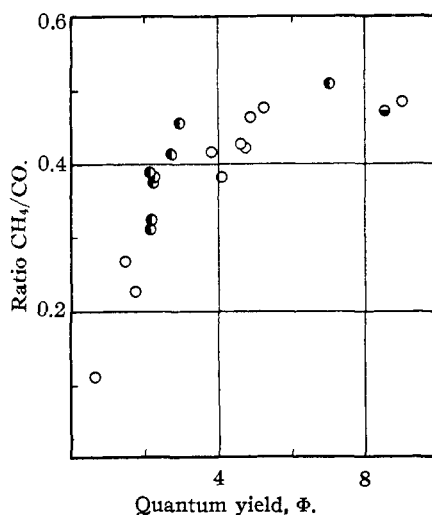

Fig. 2.—Correlation of quantum yield and CH_4/CO ratio: O, λ = 2654 Å.; ●, λ = 3130 Å.; ◖, λ = 3660 Å.

quantum yield. Despite wide variations in temperature, wave length, intensity, and pressure, there is a definite correlation between quantum yield and percentage of methane produced.

TABLE I

TYPICAL RESULTS SHOWING VARIATIONS ON COMPOSITIONS OF GASEOUS PRODUCTS WITH WAVE LENGTH AND TEMPERATURE

Run	λ, Å.	T, °C.	P, mm.	% CO	% CH_4	% C_2H_6	Ratio CH_4/CO
7	2654	25	41	73.6	8.1	13.8	0.11
5	2654	179	41	64.6	27.0	5.5	.42
18	3660	179	40	64.8	24.6	6.6	.38
25	3660	262	40	62.1	31.7	2.8	.51
R & W[a] thermal		430	380	56.3	33.7	2.7	.60

[a] Data from Rice and Walters[4a] showing the average results of four runs at 424–436°.
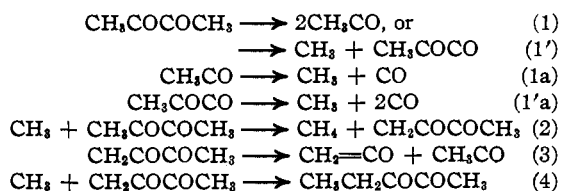
Discussion of Results

The presence of appreciable quantities of methane in the products precludes the possibility of the photolysis being due solely to a simple splitting of biacetyl directly to give ethane and two molecules of carbon monoxide. The fact that the quantum yield is several times two in certain experiments indicates that a chain process is involved. The thermal decomposition is reported to be inhibited by propylene,[4b] showing that it too proceeds through a chain mechanism. As the temperature is increased, composition of the gases from photolysis approaches the percentages found in the thermal products (Table I), indicating a similarity in reaction at higher temperatures, independent of whether initial activation was thermal or photochemical. With rise in temperature the quan-

tum yield increases, probably due to lengthening of one or more free radical chains that may occur at all temperatures studied. However, there is no evidence which rules out the possibility of a competition between a free radical mechanism and a direct fission into ethane and carbon monoxide and, as a matter of fact, the higher percentages of ethane at lower temperatures could be explained by the predominance of such a reaction.

Except for a shift into the visible region, the absorption spectrum[9] of biacetyl is rather like that for most compounds containing the carbonyl group. Under the same intensity of quanta absorbed per second, the shorter wave lengths give higher quantum yields, as would be expected in a spectrum becoming more diffuse toward shorter wave lengths.

The decrease in Φ with increase in absorbed intensity is not as great as it should be if it were proportional to $(I_a)^{-1/4}$. Over the rather narrow ranges used there was no marked variation of Φ with pressure, although there was a tendency toward slight rise with increased pressure.

For the thermal decomposition Rice and Walters[4a] have suggested the following detailed series of reactions:

$$CH_3COCOCH_3 \longrightarrow 2CH_3CO, \text{ or} \qquad (1)$$
$$\longrightarrow CH_3 + CH_3COCO \qquad (1')$$
$$CH_3CO \longrightarrow CH_3 + CO \qquad (1a)$$
$$CH_3COCO \longrightarrow CH_3 + 2CO \qquad (1'a)$$
$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_4 + CH_2COCOCH_3 \quad (2)$$
$$CH_2COCOCH_3 \longrightarrow CH_2{=}CO + CH_3CO \qquad (3)$$
$$CH_3 + CH_2COCOCH_3 \longrightarrow CH_3CH_2COCOCH_3 \quad (4)$$

This scheme must be modified or extended to account for the appreciable percentage of ethane found in the photochemical reaction, especially at lower temperatures. It is generally believed that a free radical does not readily break a C–C bond in a complete molecule. For this reason production of ethane by the reaction

$$CH_3 + CH_3COCOCH_3 \longrightarrow C_2H_6 + CH_3COCO$$
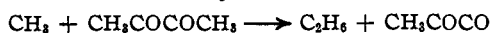
is not considered to be very probable. However, breaking of a C–C bond in a radical is not so difficult and the reaction

$$CH_3 + CH_3CO \longrightarrow C_2H_6 + CO \qquad (5)$$

may be quite likely, providing concentrations of the two radicals are sufficiently high. If ethane were produced solely by this last reaction, one would expect practically none to be formed above

(9) Sponer, "Molekülspektren," Verlag von Julius Springer, Berlin, Vol. I. 1935. p. 117.

about 100°, since the acetyl radical is quite unstable at elevated temperatures,[1,8] decomposing according to equation (1a). A reaction that has some recent support is the direct combination of two methyl radicals to form ethane,

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (6)$$
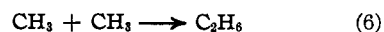
Grahame and Rollefson have evidence[10] indicating that (6) is rather accurately bimolecular. In the present work on biacetyl the termination of a short chain by this reaction would account qualitatively for the amounts of ethane formed. With the information now at hand it is perhaps unwise to comment upon the relative importance of reactions (5) and (6) except to state that with increase of temperature the occurrence of (5) becomes less probable.

A short chain involving reactions (2), (3), (1a), and (5) or (6) would give products consistent with those determined analytically and would account for variations in composition of the gas with change of temperature. Rise in temperature is accompanied by higher quantum yields (longer chains) and higher percentages of methane.

No attempt will be made to explain the small quantities of hydrogen (ca. 1.5%) and of unsaturated compounds (< 1.0%) in the gaseous product until more is known of the condensable materials produced in the reaction.

Summary

1. The photolysis of biacetyl vapor has been studied in the near ultraviolet over a temperature range 25–262°, and under varied conditions of pressure, intensity of incident radiation, and wave length.

2. Quantum yields, based on molecules of carbon monoxide produced, vary from 0.6 at room temperature to 9.0 at 260°.

3. The gaseous products were found to consist chiefly of carbon monoxide, methane and ethane. At elevated temperatures methane predominates over ethane, the ratio being about 3 to 1. Traces of hydrogen and unsaturated gases were detected.

4. A comparison is made with published results on the thermal decomposition of biacetyl. The latter mechanism is extended to explain certain photochemical results.

(10) Grahame and Rollefson, J. Chem. Phys.. 8, 98 (1940).